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(54) Title: AROMATIC DIOL BASED URETHANEACRYLATES AND RESIN COMPOSITIONS CONTAINING THE SAME
HAVING IMPROVED WATER AND/OR CHEMICAL RESISTANCE

(57) Abstract: The present invention relates to a process for making an intermediate for making an urethaneacrylate comprising reacting at least one aromatic diol with at least one polyisocyanate; to a process for making a urethaneacrylate comprising reacting (a) at least one hydroxyalkyl acrylate or at least one hydroxyalkyl methacrylate, or mixture of at least one hydroxyalkylacrylate and at least one hydroxyalkyl methacrylate, with (b) at least one abovementioned intermediate; to a curable thermoset resin composition comprising (a) at least one abovementioned urethaneacrylate, (b) at least one vinyl monomer and (c) at least one curing agent; and to a method of imparting water and/or solvent resistance to gel coated fiber-reinforced polymers comprising (a) coating a surface of a fiber-reinforced polymer with at least one abovementioned resin composition, (b) at least partially curing the coating of step (a); and (c) applying at least one gel coat to the at least partially cured coating of step (b).

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AROMATIC DIOL BASED URETHANEACRYLATES AND RESIN COMPOSITIONS CONTAINING THE SAME HAVING IMPROVED WATER AND/OR CHEMICAL RESISTANCE.

5 This invention relates to hybrid resins derived from aromatic diols, polyisocyanates and hydroxyl-terminated (meth)acrylates. This invention also relates to resin compositions having low volatile organic compound (VOC) and used as barrier coats for composite materials used in water or high moisture environments such as boat
10 hulls, watercraft frames, and swimming pool linings.

The development of composite materials with improving blister resistance has been desired for the composite industry. The blisters form when the gel-coated laminates are continuously exposed to water. The blister
15 allowing direct water contact with the laminate will, at worst, eventually lead to reduced composite strength.

Several methods have been proposed to prevent blisters in gel coated composites. U.S. Patent 4,724,173 discloses using a permeable gel coat which will allow the
20 osmotically active molecules to diffuse from the osmotic centers through the gel coat at a defined transport rate whereby blistering of the gel coat is prevented. U.S. Patent 4,477,325 discloses a method of manufacturing a skin barrier, which has superior water resistance and will
25 protect the composite material from hydrolysis.

The most common technique used by the composite industry is to use a superior corrosion or water resistance resin, such as vinyl ester resin or isophthalic polyester resin in the laminate construction. Similar
30 blister resistance is also observed if the vinyl ester resin is only used as a skin laminate or barrier coat between gel coat and main laminate. U.S. Patents 4,480,077 and 4,525,544 describe the vinyl ester resin composition, and U.S. Patent 4,959,259 describes a bisphenolic
35 polyester resin composition which can be used for this type of application. U.S. Patent 4,587,322 and European Patents 203,361 and 254,232 describe a hydroxyl functional

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urethane-extended polyester, which has superior water resistance and improved weathering characteristics. U.S. Patent 5,780,546 describes a di-alkoxylated bisphenol-A dimaleate urethane dimethacrylate hydrid resin for
5 fiberglass reinforced plastic applications.

Although blister resistance is improved using the above prior art methods, further improvements are desired in this field of use, particularly when composite materials are continuously exposed to water or extremely
10 humid conditions for prolonged periods of time, such as continuous exposure for more than six months, such as a year or more. There also continues to be a need to improve chemical resistance. The present invention addresses this need in the industry.

15 The present invention resolves the need for improved water and/or chemical resistance by applying a resin composition containing the urethaneacrylates of the present invention as a barrier coat between the gel coat and the composite material.

20 One aspect of this invention is a method for imparting water and/or solvent resistance to gel coated fiber-reinforced polymers comprising :

- (a) coating a surface of a fiber-reinforced polymer with at least one resin composition containing the
25 urethaneacrylates according to the present invention;
- (b) at least partially curing the coating of step (a) ; and, optionally,
- (c) applying at least one gel coat to the at least partially cured coating of step (b).

30 Another aspect of this invention is the gel coated products of the foregoing method.

Yet another aspect of this invention is curable thermoset resin compositions comprising at least one urethaneacrylate according to the present invention ; at
35 least one vinyl monomer ; and at least one curing agent. The at least one urethaneacrylate according to the present invention is obtainable by reacting at least one

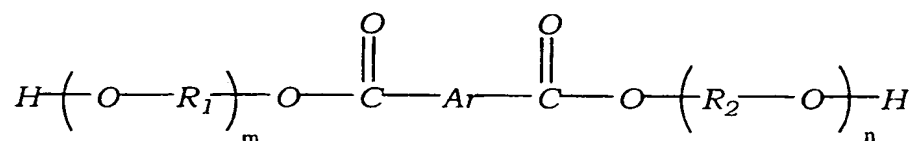
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hydroxyalkyl acrylate or at least one hydroxyalkyl methacrylate, or mixture of at least one hydroxyalkyl acrylate and at least one hydroxyalkyl methacrylate, with at least one intermediate obtainable by reacting at least one aromatic diol with at least one polyisocyanate.

The processes for making the intermediates and urethaneacrylate products, and the products obtainable thereby, are additional aspects of this invention.

The process for making the urethaneacrylates of the present invention begins with reacting at least one aromatic diol with at least one polyisocyanate to form an intermediate. The at least one aromatic diol may be selected from a wide range of compounds having at least one aromatic group and two hydroxy groups capable of reacting with the at least one polyisocyanate compound preferably at a temperature below the decomposition temperature of the intermediate. The aromatic groups are preferable substituted or unsubstituted phenyl groups, wherein the substituted phenyl groups are preferably substituted with one or more hydrocarbyl groups, hetero groups and hetero atoms. The hydroxy groups from the aromatic diol could be either primary or nonprimary. The hydroxy groups are preferably each attached to the aromatic groups via a separate divalent linking group comprising carbon atoms and hydrogen atoms, and optionally hetero atoms, such as oxygen. The hydroxy groups are preferably terminal hydroxy groups. In one preferred embodiment, the linking group comprises alkenyloxy functional units.

Examples of aromatic diols are the ones represented by the formula :



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wherein Ar represents an aromatic group ; R_1 and R_2 each independently represent a non-aromatic predominantly hydrocarbyl group ; and m and n each independently represent an integer in the range from 1 to 10.

5 Furthermore, the aromatic diol could be a mixture of more than one aromatic diol or mixture of aromatic and non-aromatic diol with the aromatic component dominating (representing more than 50% of) the mixed structure.

10 In a preferred embodiment, the at least one aromatic diol is obtainable by reacting at least one alkylene oxide with at least one of the aforementioned aromatic groups disubstituted with carboxylic acid groups, i.e., an aryl dicarboxylic acid. The alkylene oxide reactant is preferably selected from the C_2 - C_8 alkylene
15 oxides. Propylene oxide, ethylene oxide and mixtures of propylene oxide and ethylene oxide, commonly used for alkoxylation are suitable. The carboxylic groups are groups that contain at least one carboxylic acid functional group $-C(O)OH$ and/or an anhydride, salt or
20 ester thereof and which may or may not be attached to the aromatic ring via a linking group comprising carbon atoms and hydrogen atoms, and optionally, hetero atoms. Examples of carboxylic groups include $-C(O)OH$, $-C(O)O(O)C-$. The carboxylic acid functional group $-C(O)OH$
25 is preferred. Preferred examples of suitable aryl dicarboxylic acids include isophthalic acid and terephthalic acid. The molar ratio of the alkylene oxide to carboxylic acid groups on the aryl dicarboxylic acid is preferably in the range from about 0.1:1 to about 10:1,
30 and more preferably from about 0.5:1 to about 5:1. The reaction temperature is preferably in the range from about $50^\circ C$ to about $200^\circ C$, more preferably from about $75^\circ C$ to about $150^\circ C$. The reaction pressures are preferably in the range from about 68.95 kPa (10 psi) to about 2758 kPa
35 (400 psi), more preferably in the range from about 13.79 kPa (20 psi) to about 689.5 kPa (100 psi). The reaction time is preferably in the range from about

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20 minutes to about 20 hours, more preferably from about 30 minutes to about 10 hours.

Specific examples of how to make aromatic diols useful for making preferred intermediates according to the present invention are provided in U.S. Patent 5,880,251, which is hereby incorporated herein by reference for its relevant disclosure (described therein as the "first stage reaction").

The polyisocyanates may be selected from a wide range of compounds having at least two isocyanate groups. The polyisocyanates preferably include aliphatic polyisocyanates and aryl polyisocyanates. Examples of suitable preferred aliphatic polyisocyanates include ethylene diisocyanate, hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), cyclohexane-1,4-diisocyanate, methylene bis(4-cyclohexylisocyanate) (HMDI), and Luxate HB9000 (HDI biuret) obtainable from Lyondell Chemical Company. Examples of preferred aryl polyisocyanates include 2,4-toluene diisocyanate (TDI), 2,6-toluene diisocyanate, diphenylmethane 4,4-diisocyanate (MDI), xylylene diisocyanate, and 1,4-phenylene diisocyanate. The molar ratio of the hydroxy groups on the aromatic diol to isocyanate groups on the polyisocyanate is preferably in the range from about 0.1:1 to about 10:1, and more preferably from about 0.25:1 to about 4:1. The reaction temperature is preferably in the range from about 0° to about 150°C, more preferably from about 20° to about 120°C.

The above intermediates of this invention are useful for making urethaneacrylates according to the present invention. The urethaneacrylates are obtainable by reacting at least one intermediate with at least one hydroxyalkyl acrylate or at least one hydroxyalkyl methacrylate, or mixture of at least one hydroxyalkyl acrylate and at least one hydroxyalkyl methacrylate. The ester alkyl group may be selected from any C₁-C₈ alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl,

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etc. Examples of preferred hydroxyalkyl methacrylates are 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), 2-hydroxypropyl methacrylate (HPMA), 2-hydroxypropyl acrylate (HPA), 2-hydroxybutyl (meth)acrylate, and 2-hydroxy-3-phenyloxypropyl (meth)acrylate. The molar ratio of the hydroxy groups on the hydroxyalkyl (meth)acrylates to isocyanate groups on the intermediate is preferably in the range from about 0.1:1 to about 10:1, and more preferably from about 0.25:1 to about 4:1. The reaction temperature is preferably in the range from about 0°C to about 150°C, more preferably from about 20°C to about 120°C.

It is also known to the industry that the polyisocyanate could react with at least one hydroxyalkyl acrylate or at least one hydroxyalkyl methacrylate, or mixture of at least one hydroxyalkyl acrylate and at least one hydroxyalkyl methacrylate to form an intermediate. The intermediate is then reacting with the aromatic diols to form the urethaneacrylates. It is also known to the polyurethane industry that polyols other than the aromatic diols can be used to modify the properties of urethaneacrylates. Polyols may be polyols with a number average molecular weight of about 200 to 10,000 such as polyether polyols, polyester polyols, polyesteramide polyols, polycarbonate polyol, urethanated polyol, polyacetal polyols, polyolefin polyols, polysiloxane polyols, and the like.

The urethaneacrylates of the present invention are useful for making curable thermoset resin compositions. The curable thermoset resin compositions generally comprise at least one urethaneacrylate according to the present invention, at least one vinyl monomer, and at least one curing agent and are obtainable by blending these components, and any optional additional components, of the curable thermoset resin composition.

The vinyl monomer may be any vinyl monomers which are capable of reacting with the vinyl groups of the at

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least one urethaneacrylate. Examples of such monomers include styrene, vinyl toluene, p-methyl styrene, chlorostyrene, t-butyl styrene, diallyl phthalate, mono- or multifunctional lower alkyl esters of acrylic or methacrylic acids such as methyl methacrylate and glycol diacrylate and the like. Styrene is preferred.

The curing agent may be any agent that catalyzes free radical reactions in resin compositions. Useful free radical initiators are those well known and commercially available in the unsaturated polyester industry. They include peroxide and azo-type initiators. Peroxide initiators include, for example, methylethyl ketone (MEK) peroxide, benzoyl peroxide, tert-butylperbenzoate, tert-butylperoxide, and the like, and mixtures thereof. An example of a commercially available initiator is THERMOCURE® JTS (a methylethyl ketone peroxide available from Cook Composites and Polymers, Inc.). The initiator is used in an amount effective to react the vinyl aromatic monomer and their polymer components of the curable thermoset resin composition to produce a cured thermoset. Typically, the amount is within the range from about 0.5 to about 3 wt.%, more preferable from about 1 to about 2 wt.%, based on the curable thermoset resin composition.

The curable thermoset resin compositions of this invention may optionally contain additional components, such as one or more fillers, one or more pigments, and one or more performance enhancing additives. Examples of performance enhancing additives include air release agent, rheology modifier, promoter, and inhibitors. These additives are known to the composite industry.

In a preferred embodiment, the curable thermoset resin composition contains at least about 40 wt.%, more preferably at least about 50 wt.%, and/or up to about 90 wt.%, more preferably up to about 80 wt.%, of at least one urethaneacrylate according to this invention. In the same or different preferred embodiment, the curable thermoset resin composition contains at least about 10 wt.%, more

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preferably at least about 20 wt.%, up to about 50 wt.%, more preferably up to about 35 wt.%, of at least one vinyl monomer. In the same or different preferred embodiment, the curable thermoset resin composition contains at least
5 about 0.5 wt.%, more preferably at least about 1 wt.%, and/or up to about 3 wt.%, more preferably up to about 2 wt.%, of at least one curing agent.

In the same or a different preferred embodiment, the curable thermoset resin composition optionally
10 contains up to about 40 wt.%, more preferably up to about 30 wt.%, of at least one filler.

In the same or a different preferred embodiment, the curable thermoset resin composition optionally contains up to about 5 wt.% of at least one pigment.

15 The weight ratio of urethaneacrylate to vinyl monomer in the curable thermoset resin composition is preferably at least about 2:3, more preferably at least about 1:1 and/or up to about 9:1, more preferably up to about 4:1.

20 The curable thermoset resin compositions of this invention are useful for imparting water and/or solvent resistance to gel coated fiber-reinforced polymers. One approach to obtaining this benefit comprises :

- a) coating a surface of a fiber-reinforced polymer with
25 at least one resin composition containing the urethaneacrylates, such as the curable thermoset resin compositions according to the present invention;
- b) at least partially curing the coating of step (a) ;
30 and, optionally,
- c) applying at least one gel coat to the at least partially cured coating of step (b)

The advantage of interposing the thermoset resin of the present invention as a barrier coat between a gel
35 coat layer and the fiber-reinforced polymer layer is the prevention, or minimization, of blistering due to the migration of water and/or other low molecular weight

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substances, such as organic solvents, through the gel coat into the fiber-reinforced polymer layer, causing swelling, delamination, and other problems in the fiber-reinforced polymers layer. The swelling can cause a blister under the gel coat and continued migration of water and/or other solvents into the fiber-reinforced polymer can eventually lead to loss of strength in the fiber-reinforced polymer laminate.

In one embodiment, blistering of a gel coated fiber-reinforced polymer is reduced by applying at least one layer of the curable thermoset resin composition between the gel coat layer and the fiber-reinforced polymer layer and curing the curable thermoset resin composition. Preferable, this is carried out by applying a gel coat composition to a mold, applying at least one curable thermoset resin composition to the gel coat, at least partially curing the curable thermoset resin composition, applying at least one fiber-reinforced polymer layer to the at least partially cured thermoset resin composition layer, and curing the resulting product to form the gel coated fiber-reinforced polymer.

The gel coat composition may be any of those that are well known and available in the art. The gel coat is typically 0.25 to 0.5 mm (10 to 20 mils) in thickness, and is the surface coating of the molded part. The thickness of the curable thermoset resin composition useful for imparting water and/or solvent resistance is typically 0.2 to 0.75 mm (10 to 30 mils) in thickness.

The composite and the molded part can, and often are, constructed in one operation. First, a gel coat is usually applied to the surface of the mold, and then a barrier coat is applied over the gel coat. These are open mold operation. Then the fiber-reinforced polyester matrix precursor is applied, for example, by hand lay-up or spray-up, or the fiber reinforcement is applied to the skin laminate, the mold is closed, and the polyester matrix precursor is injected into the closed mold,

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preferably with the closed mold under vacuum. The precursor is then allowed to cure, with or without a heat supplement, and the part or article demolded.

Products which have the resin compositions of this invention as a barrier coat between a gel coat and a main laminate have a high degree of blister resistance and excellent laminate profile appearance over the conventional unsaturated polyester resins. The resin compositions of this invention provide a more durable laminate structure and the composite structure requires less repair over the service life of the composite structure. In a preferred embodiment, the product has an American National Standards Institute ("ANSI") Blister Rating of not greater than about 2.0, more preferably not greater than about 1.5, and/or an ANSI Total Rating of not more than about 3.5, more preferably not greater than about 3.0, for a 100 hour water boil panel prepared as described in the "Hydrolytic Stability Test Protocol" below.

Hydrolytic Stability Test Protocol

The gel coat laminates are prepared by first spraying a full ISO/NPG type of gel coat on a glass mold and drawing down to 0.58 mm (23 mils) and 1.22 mm (48 mils) "wet" thickness. Then a layer of barrier coat about 0.51 mm (20 mils) "wet" is applied to the gel coat. The gel coat and barrier coat is cured for at least 1 hour at ambient temperature before putting on the main laminate. A typical marine grade laminate resin having a glass content of about 35 wt.% is applied at a thickness of about 0.635 cm (0.25 inches). The laminate is cured at ambient temperature for at least 16 hours before the water boil test is performed. The panel is exposed to boiling water for 100 hours and then the ANSI Blister Rating and ANSI Total Rating are measured according to the protocol described in ANSI publication Z124.1-1987, section 6.3.

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The following examples are provided for the purpose of illustrating the invention. They are not to be construed as limiting the scope of the invention which is defined by the appended claims.

Examples

Preparation of aromatic diols

10

Bis-hydroxypropyl isophthalate ("isodiol") and bis-hydroxypropyl terephthalate ("terediol") are prepared following the teaching described in U.S. patent 5,880,251. The production of isodiol is described here. The following ingredients were introduced into a two-gallon stainless steel autoclave : 15 grams benzyltriethylammonium chloride, 1800 grams isodiol, and 2000 grams of isophthalic acid. The air in the autoclave was completely replaced by the introduction of nitrogen gas and the mixture was heated to 125°C. 1400 grams of propylene oxide was then continuously added over 160 minutes at a stirring rate of 100 rpm while maintaining a reaction temperature in the autoclave of 125°C and a reactor pressure below 0.345 MPa (50 psi). After completion of the propylene oxide addition, the reaction was continued at 125°C for an additional 60 minutes at a pressure below 0.345 MPa (50 psi). The reaction product was then purged with nitrogen. 5060 grams of the isodiol having an acid value of 12 (mg KOH/g) was obtained.

30

Example A

Into a 1-liter flask equipped with agitator, condenser, thermometer, and pipe for introducing nitrogen gas were charged 366 grams of isodiol, 0.4 grams of hydroquinone (HQ), and 494 grams of styrene. The mixture was well stirred until it formed a homogeneous solution.

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454 grams of TDI (Bayer, MONDUR TD-80) was added into the solution at the ambient temperature, and the mixture was heated to 50 to 60°C and held for three hours. 412 grams of HEMA was then added into the flask, and the temperature was increased to 60 to 70°C. The reaction was completed when no isocyanate can be detected from the product. The determination of residual isocyanate can be through titration or through infrared spectroscopy.

10 Example B

Into a 1-liter flask equipped with agitator, condenser, thermometer, and pipe for introducing nitrogen gas were charged 283 grams of isodiol, 0.4 grams of hydroquinone (HQ), and 370 grams of styrene. The mixture was well stirred until it formed a homogeneous solution. 348 grams of TDI (Bayer, MONDUR TD-80) was added into the solution at the ambient temperature, and the mixture was heated to 50 to 60°C and held for three hours. 232 grams of HEA was then added into the flask, and the temperature was increased to 60 to 70°C. The reaction was completed when no isocyanate can be detected from the product.

Example C

Into a 1-liter flask equipped with agitator, condenser, thermometer, and pipe for introducing nitrogen gas were charged 261 grams of terediol, 0.4 grams of HQ, and 445 grams of styrene. The mixture was well stirred until it formed a homogeneous solution. 333 grams of TDI (Bayer, MONDUR TD-80) was added into the solution at the ambient temperature, and the mixture was heated to 50 to 60°C and held for three hours. 250 grams of HEMA was then added into the flask, and the temperature was increased to 60 to 70°C. The reaction was completed when no isocyanate can be detected from the product.

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Example D

Into a 1-liter flask equipped with agitator, condenser, thermometer, and pipe for introducing nitrogen gas were charged 354 grams of isodiol, 0.4 grams of HQ, and 310 grams of styrene. The mixture was well stirred until it formed a homogeneous solution. 86 grams of aliphatic diisocyanate (Lyondell, Luxate® HB9000) and 0.5 grams of dibutyltin dilaurate were added into the flask. The mixture was heated to 60 to 70°C and held for four hours. 196 grams of TDI (Bayer, MONDUR TD-80) was added into the solution and the reaction was continued at 50 to 60°C for two hours. 140 grams of HPMa was then added into the flask, and the temperature was increased to 60 to 70°C. The reaction was completed when no isocyanate can be detected from the product.

Table 1

The mechanical properties of various resin systems

	Tensile Strength in MPa (psi)	Flexural Strength in MPa (psi)	Elongation (%)	HDT (°C)
Example A	91.70 (13300)	143.8 (20860)	2.66	117
Example B	92.12 (13360)	151.6 (21990)	2.54	101
Example C	69.63 (10100)	139.8 (20270)	1.59	113
Example D	96.67 (14020)	138.5 (20090)	3.36	96

Table 1 shows a comparison of the mechanical properties of the urethaneacrylate Examples A to D according to the present. The tensile properties were obtained following the ASTM D638. The flexural properties were obtained following the ASTM D695. The HDT was obtained following ASTM D648. The urethaneacrylates of the present invention also have good water resistance and low shrinkage. The typical linear shrinkage of urethaneacrylate is less than 0.5%.

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Example F

A barrier coat is prepared by mixing the urethaneacrylate prepared in Example A with 20 wt.% alumina trihydrate (ATH), 2 wt.% black pigment, 10 wt.% styrene monomer, and curing promoters and inhibitors known to the industry. The VOC of the barrier coat is less than 34 wt.%.

Table 2 lists the surface profiles of various laminates measured by wave-scan. Laminates with the barrier coat showed significant improvement in the surface appearance over the laminate without barrier coat. Another advantage of using urethane vinyl ester in the barrier coat application is that the lower VOC type of barrier coat products can be formulated. The urethane vinyl ester resin has the VOC around 34%, which meets the MACT (maximum achievable control technology) standard of styrene emissions for marine industry.

Table 2

Surface profile of gel-coated laminates with and without barrier coat

	Example F	No barrier coat
0.58 mm(23 mils) gel coat long-term waviness	2.2	6.8
0.58 mm(23 mils) gel coat short-term waviness	4.5	4.2
0.58 mm(23 mils) gel coat surface rating	10.1	7.7
1.22 mm(48 mils) gel coat long-term waviness	0.5	1.7
1.22 mm(48 mils) gel coat short-term waviness	4.7	4.5
1.22 mm (48 mils) gel coat surface rating	10.5	10.5

Table 3 shows the surface profile of samples after the hydrolytic stability test. The results indicate

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Table 3 shows the surface profile of samples after the hydrolytic stability test. The results indicate that the urethaneacrylate type barrier coat according to the present invention has improved the hydrolytic stability of the gel coated laminate.

Table 3

ANSI* ratings for 100 hours water boil panel

10

	Example F	No barrier coat
ANSI Blister Rating	1.22	2.83
ANSI Total Rating	2.89	4.47

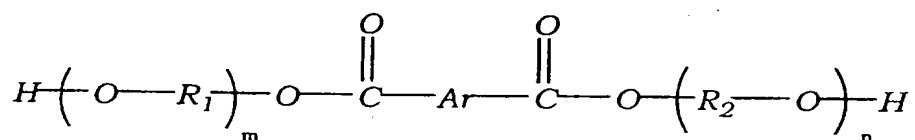
* ANSI is American National Standards Institute. The referred test is in the publication ANSI Z124.1-1987 section 6.3. Lower the ANSI rating indicates better surface profile. The ANSI rating over 9 is considered failure.

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CLAIMS

1 - A process for making an intermediate for making
 5 an urethaneacrylate comprising reacting at least one aromatic diol with at least one polyisocyanate.

2 - The process according to claim 1 wherein the at least one aromatic diol is represented by the formula :



10

wherein Ar represents an aromatic group ; R₁ and R₂ each independently represent a non-aromatic predominantly hydrocarbyl group ; and m and n each independently represent an integer in the range from 1 to 10.

15

3 - The process according to claim 1 or 2 wherein the aromatic diol could be a mixture of more than one aromatic diol or mixture of aromatic and non-aromatic diol with the aromatic component dominating the mixed structure.

20

4 - The process according to anyone of claims 1 to 3 wherein the at least one polyisocyanate is selected from the group consisting of TDI, IPDI, MDI, HDI and H-MDI and mixtures thereof.

5 - An intermediate obtainable according to any one
 25 of claims 1 to 4.

6 - A process for making a urethaneacrylate comprising reacting (a) at least one hydroxyalkyl acrylate or at least one hydroxyalkyl methacrylate, or mixture of at least one hydroxyalkyl acrylate and at least one
 30 hydroxyalkyl methacrylate, with (b) at least one intermediate of claim 5.

7 - The process according to claim 6 wherein the at least one hydroxyalkyl acrylate is selected from HEA and

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HPA and the at least one hydroxyalkyl methacrylate is selected from HEMA and HPMA.

8 - An urethaneacrylate obtainable according to claim 6 or 7.

5 9 - A curable thermoset resin composition comprising:

(a) at least one urethaneacrylate according to claim 8 ;

(b) at least one vinyl monomer ; and

(c) at least one curing agent.

10 10 - The resin composition of claim 9 containing at least 40 wt.% of the at least one urethaneacrylate.

11 - The resin composition of claim 9 or 10 further comprising a filler.

15 12 - A method of imparting water and/or solvent resistance to gel coated fiber-reinforced polymers comprising :

(a) coating a surface of a fiber-reinforced polymer with at least one resin composition according to any one of claims 9 to 11 ;

20 (b) at least partially curing the coating of step (a) ; and

(c) applying at least one gel coat to the at least partially cured coating of step (b).

25 13 - The gel coated product of the method according to claim 12.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/10721

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/67 C08G18/42 C09D175/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 25 42 314 A (TOYO BOSEKI) 15 April 1976 (1976-04-15) page 5, line 3 -page 10, line 7; claims 1-13; examples	1-10
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X	EP 0 102 312 A (GOODYEAR TIRE AND RUBBER) 7 March 1984 (1984-03-07) page 2, line 10 -page 5, line 31; claims 1-10; example 4	1-10
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

21 February 2001

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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